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(54) **Process for producing a silicone polymer**

Verfahren zur Herstellung eines Siliconpolymeren

Procédé de préparation d'un polymère silicone

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EP-A- 0 985 347 **GB-A- 2 154 596**
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Description

[0001] The present invention relates to a process for producing a silicone polymer having low volatile material content by polymerisation of siloxanes, in the presence or absence of a filler, catalysed by a phosphazene base.

[0002] Cyclosiloxanes are critical intermediates in the silicone industry, primarily as starting materials for polymerisation reactions. Several general routes are known for the preparation of cyclosiloxanes. Together with hydroxy-end-blocked linear polydiorganosiloxanes, they are formed as a product of hydrolysis of corresponding diorganodihalosilanes.

[0003] Various catalysts are known for the polymerisation of cyclosiloxanes. Examples are alkali metal hydroxides, alkali metal alkoxides or complexes of alkali metal hydroxides and an alcohol, alkali metal silanates, and phosphonitrile halides (sometimes referred to as acidic phosphazenes). Such polymerisation reactions can be carried out substantially in the absence of solvent, in solvents (such as non-polar or polar organic solvents) or in emulsion. An end-blocking agent may be used to regulate the molecular weight of the polymer and/or to add functionality, for example to add vinyl functional end groups. Polymerisation may be terminated by using a neutralising agent which reacts with the catalyst to render it non-active. In most cases catalyst residues and salts following neutralisation remain in the polymer product which may cause some re-equilibration of silicone polymer back to the siloxane starting materials. These residues and salts are desirably removed, such as by filtration. Volatile materials, including cyclosiloxanes, are removed from the silicone polymer by stripping, typically at temperatures of from 120 to 200°C and under reduced pressure of 200 to 20000 Pa, to afford a silicone polymer having a volatile material content of typically from 1.0 to 5% by weight. Stripping under more extreme conditions can cause decomposition of the silicone polymer.

[0004] Another known process for producing a silicone polymer by polymerisation of siloxanes is condensation polymerisation of silanol or other hydrolysable group containing linear siloxanes. For example, in GB 2311994 there is described a method of effecting polycondensing which comprises contacting at a temperature of from 0 to 200°C and a pressure up to 4.67×10^{-4} Nm⁻², a silanol-containing organosiloxane with an amount of a peralkylated phosphazene base which is effective for polycondensation of said organosiloxane. The preferred peralkylated phosphazene base has the formula $R^{\#}N=P\{N=P(NR^*_{2})_{3}\}_n\{R^{\#}_{2}N\}_{3-n}$ wherein R[#] is a C₁₋₄ alkyl radical, R* is a C₁₋₁₀ alkyl radical and n is 2 or 3.

[0005] Phosphazene bases are known to be extremely strong bases. Numerous phosphazene bases and routes for their synthesis have been described in the literature, for example in Schwesinger *et al*, *Liebigs Ann.* 1996, 1055-1081.

The use of a phosphazene base catalyst for the ring-opening polymerisation of a cyclosiloxane on a laboratory scale has been described in Molenberg and Möller, *Macromol Rapid Commun.* 16, 449-453 (1995). Octamethylcyclotetrasiloxane (D4, where D denotes an -Si(CH₃)₂O- unit) was polymerised in toluene solution in the presence of methanol and the phosphazene base I described hereinbelow, used as a 1 molar solution in hexane. All the components were carefully dried before the reaction, which was carried out under an argon atmosphere containing less than 1ppm O₂ and H₂O. The methanol was deprotonated by the phosphazene base to form methoxide ions which initiate the reaction. The phosphazene base catalyst was used in an amount of at least 871ppm based on the weight of D4. A similar reaction system has been used by Van Dyke and Clarson in *Poly Prep ACS Div Polym Chem* 1996, 37, 668. In this case, tetraphenyltetramethylcyclotetrasiloxane, the phenylmethyl analog of D4, was polymerised. The catalyst system was the same as in Molenberg and Möller, but was used at concentrations which were higher based on the weight of D4, and again all the reaction components were carefully dried beforehand.

[0006] The present inventors have found that addition of this hexane/methanol activated catalyst gives erratic polymerisation behaviour. They therefore sought a catalyst medium that gives reproducible polymerisation, preferably without the need for solvent, and surprisingly found that it is possible to carry out polymerisation of siloxanes with a phosphazene base catalyst in the presence of water. To ensure the presence of water it is sufficient to avoid totally anhydrous conditions. Very small amounts of water, e.g. a few molecules, have been found to suffice to allow the polymerisation to take place. Furthermore, the present inventors found that it is not essential to form a methoxide ion, e.g. by using methanol, in contrast to the prior art teaching. Surprisingly, even lower levels of phosphazene base catalyst can be used where water is present, than were used in the prior art, whilst maintaining or improving the polymerisation efficiency.

[0007] Polymerisation of siloxanes may occur in the presence of a filler. Silicone polymer-filler mixtures are known for use as bases for various silicone rubber compositions, silicone compounds and greases, etc. Conventional mixtures are generally produced by first polymerising silicone oligomer into a silicone polymer with the desired viscosity and then mechanically mixing the resulting silicone polymer with the selected filler. However, such methods involve two different types of processes, necessitating a separate polymerisation step and mixing step.

[0008] As a result, the process is complicated and disadvantageous on a cost basis. In addition, it is difficult in such methods to mix and disperse filler into high-viscosity silicone polymers and large amounts of energy are consumed. This problem becomes particularly significant when the molecular weight of the silicone polymer is as high as that of a so-called gum.

5 [0009] Attempts have been made to overcome these problems by carrying out the polymerisation in the presence of the filler. US-A-4 448 927 discloses a method of polymerising a hydroxy-endblocked polydiorganosiloxane and/or a polydiorganocyclosiloxane in the presence of an acidic or neutral reinforcing filler and catalysed by trifluoromethane sulfonic acid. EP-A-0 119 816 discloses a method of bulk polymerisation of a hydroxy-endblocked polydiorganosiloxane and/or a polydiorganocyclosiloxane in the presence of an acidic or neutral reinforcing filler and catalysed by sulfuric acid or a sulfonic acid. EP-A-0 119 093 discloses a method of polymerising a hydroxy-endblocked polydiorganosiloxane in the presence of an inorganic reinforcing or extending filler and a basic diorganosilanolate catalyst. GB2154596 describes a continuous production of silicone gums comprising a process comprising heating a mixture of one or more cyclopolysiloxane monomers with chain-stopping agents adding catalyst polymerising the resulting mixture in a screw extruder having plug flow therethrough and the neutralising the catalyst in the polymer. The exemplified catalyst is potassium silanolate. EP 0119092 describes method of polymerising hydroxyl endblocked polydiorganosiloxanes using a catalyst mixture of quaternary ammonium carboxylate and carboxylic acid. US-A-4 431 771 discloses the polymerisation of a hydroxy-endblocked polydiorganosiloxane in the presence of an acidic or neutral reinforcing filler and a catalyst selected from sulfuric acid, sulfonic acids, perfluorinated alkane sulfonic acid, and a combination of quaternary ammonium carboxylate and carboxylic acid. While these processes have been successful with linear starting materials, they have been less successful with cyclosiloxanes, as the rates of polymerisation have generally been regarded as too slow.

[0010] Thus, the present inventors have found that phosphazene base catalysts are well suited for polymerisation of siloxanes in the presence or absence of fillers.

20 [0011] The present inventors have found that silicone polymers made by polymerisation of siloxanes catalysed by phosphazene bases have enhanced thermal stability over silicone polymers made using conventional catalysts. This enhanced thermal stability is attributed to the very low levels of catalyst residues remaining in the product after catalyst neutralisation. Thus, stripping of silicone polymers having enhanced thermal stability may be effected at correspondingly higher temperatures than those used for stripping silicone polymers made using conventional catalysts, which results in correspondingly lower volatile materials content in the final silicone polymer. The low levels of catalyst residues also mean that a filtration step is usually not necessary.

25 [0012] For the avoidance of any doubt, use of the concept of "comprising" herein means "consisting of" and "including".

30 [0013] According to the present invention there is provided a process for producing a silicone polymer having a volatile material content of less than 1% by weight which process comprises the sequential steps of (i) producing an unstripped silicone polymer by polymerisation of a linear silanol group containing siloxane by condensation polymerisation, or of a cyclosiloxane by ring-opening polymerisation, or of a mixture of said linear and cyclosiloxanes, with a phosphazene base in an amount of from 1 to 750ppm by weight based on weight of siloxane in the presence of at least 0.5mols of water per mol of phosphazene base and the presence or absence of a filler, (ii) neutralising the catalyst, and (iii) stripping the unstripped silicone polymer.

35 [0014] For the avoidance of any doubt, use of the word "comprises" herein means "consists of or includes".

[0015] Herein the term "volatile material" means fluid material having a boiling point lower than the decomposition temperature of the silicone polymer. This fluid material is mixed with the silicone polymer and is present as a result of the polymerisation reaction. The volatile material substantially consists of unreacted siloxane starting material, but will also include minor amounts of other materials such as solvents and water.

40 [0016] Silicone polymers produced according to the process of the present invention have a volatile material content of less than 1% by weight, preferably 0.5% by weight or less, more preferably 0.1% by weight (1000ppm by weight) or less, (for example, from 0.01 to 0.1% by weight (100 to 1000ppm) by weight), most preferably 0.01% by weight (100ppm by weight) or less. This compares to typical volatile material content of from 1.0 to 5.0% by weight for silicone polymers produced using conventional catalysts.

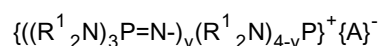
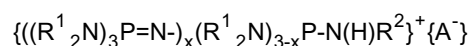
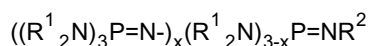
45 [0017] In step (i) of the process of the present invention, the phosphazene base reacts with trace quantities of water present to form highly active hydroxide ions which initiate the polymerisation. The phosphazene base will also react with certain other chemical groups which may be present, e.g. silanol or alcohol, to form similarly active polymerisation-initiating species. The phosphazene base may be in ionic form, with a strong anion such as fluoride or hydroxide, which is active in initiating polymerisation.

50 [0018] As the phosphazene base is a very powerful catalyst for the polymerisation it can be present in a relatively low proportion, for example 1 - 750 ppm by weight based on the weight of siloxane. A preferred range is 1 - 500 ppm by weight, more preferably 10 - 100 ppm. The proportion of catalyst actually used will be selected depending on the polymerisation product that is sought.

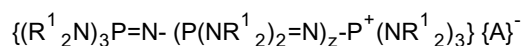
55 [0019] In the simplest case, sufficient water can be provided for the ring-opening polymerisation reaction simply by taking no special steps to dry the filler or the siloxane starting material. The proportion of water present in the reaction is preferably at least 0.5, more preferably from 0.5-10, mols per mol of phosphazene base, most preferably from 1-10 mols per mol of phosphazene base. It is possible to employ higher proportions of water, and this can have the benefit

of enabling greater control over the polymerisation reaction, as described in more detail below.

[0020] In principle, any phosphazene base is suitable for use in the present invention. Phosphazene bases have the following core structure P=N-P=N, in which free N valencies are linked to hydrogen, hydrocarbon, -P=N or =P-N, and free P valencies are linked to -N or =N. A wide range of suitable phosphazene bases has been described in Schwesinger *et al* (see above). Some phosphazene bases are commercially available from Fluka Chemie AG, Switzerland. The phosphazene bases preferably have at least 3 P-atoms. Some preferred phosphazene bases are of the following general formulae:

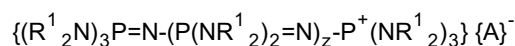


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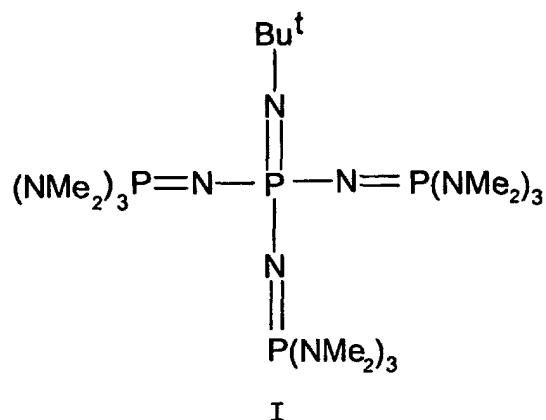
in which R¹, which may be the same or different in each position, is hydrogen or an optionally substituted hydrocarbon group, preferably a C₁-C₄ alkyl group, or in which two R¹ groups bonded to the same N atom may be linked to complete a heterocyclic ring, preferably a 5- or 6-membered ring; R² is hydrogen or an optionally substituted hydrocarbon group, preferably a C₁-C₂₀ alkyl group, more preferably a C₁-C₁₀ alkyl group; x is 1, 2 or 3, preferably 2 or 3; y is 1, 2, 3 or 4, preferably 2, 3 or 4; z is an integer of from 1 to 10, preferably 1, 2, or 3; and A is an anion, preferably fluoride, hydroxide, silanolate, alkoxide, carbonate or bicarbonate.

[0021] The compounds of the formula



may be made by a method which comprises reacting a linear phosphonitrile halide compound, preferably chloride, with a compound selected from a secondary amine, a metal amide and a quaternary ammonium halide to form an aminated phosphazene material, followed by an ion exchange reaction replacing the anion with a nucleophile. Phosphonitrile halide compounds and methods of making them are well known in the art; for example, one particularly useful method includes the reaction of PCl₅ with NH₄Cl in the presence of a suitable solvent. Secondary amines are the preferred reagent for reaction with the phosphonitrile halide, and a suitable secondary amine has the formula R³₂NH, wherein R³ is a hydrocarbon group having up to 10 carbon atoms, or both R³ groups form a heterocyclic group with the nitrogen atom, for example a pyrrolidine group, a pyrrole group or a pyridine group. Preferably, R³ is a lower alkyl group, more preferably a methyl group, or both R³ groups form a pyrrolidine ring. Suitable preferred secondary amines include dimethylamine, diethylamine, dipropylamine and pyrrolidine. Preferably the reaction is carried out in the presence of a material which is able to capture the exchanged halides, e.g. an amine such as triethylamine. The resulting by-product (e.g. triethyl ammonium chloride) can then be removed from the reaction mixture, e.g. by filtration. The reaction may be carried out in the presence of a suitable solvent for the phosphonitrile chloride and linear phosphazene base. Suitable solvents include aromatic solvents such as toluene. The linear phosphazene material which is formed this way must then be passed through an ion exchange reaction (preferably an ion exchange resin) whereby the anion is replaced with a hard nucleophile, preferably hydroxyl or alkoxy, most preferably hydroxyl. Suitable ion exchange systems include any known ion exchange systems, e.g. ion exchange resins, and no further detailed description is given. The phosphazene is preferably dispersed in a suitable medium prior to passing through an ion exchange system. Suitable media include water, alcohol and mixtures thereof.

[0022] In particularly preferred phosphazene base compounds for use in the present invention, R¹ is methyl, R² is tert. butyl or tert. octyl, x is 3, y is 4 and A is fluoride or hydroxide. A preferred compound is the phosphazene base I:



[0023] The polymerisation can be carried out in the absence or presence of a solvent. Suitable solvents are liquid hydrocarbons or silicone fluids. The phosphazene base catalyst can be diluted in a hydrocarbon solvent, such as hexane or heptane, or dispersed in a silicone fluid. Where the phosphazene base catalyst is initially in a solvent such as hexane, the hexane can be removed by evaporation under vacuum, and the catalyst dispersed in a silicone fluid to give a stable clear solution. When this silicone dissolved catalyst is used for polymerisation reactions, the catalyst disperses evenly and gives reproducible results. The catalyst can also be dissolved in water, and this has the advantage of moderating and enabling greater control over the polymerisation reaction, as described below.

[0024] The polymerisation reaction can be carried out at ambient temperature or under heating. Heating, for example to 100°C or higher, is appropriate when the catalyst activity has been moderated as described below. The time taken for polymerisation will depend on the activity of the catalyst in the chosen system, and on the desired polymer product. For example, in the absence of moderation, the phosphazene base catalysts are sufficiently active to convert cyclosiloxanes such as D4 to high molecular weight polysiloxane gums within a few seconds.

[0025] Starting materials for the condensation reaction of silanol containing siloxanes are organosiloxanes having silicon-bonded hydroxyl groups or hydrolysable groups such as alkoxy or aryloxy groups, which may form silanol groups in situ. These include, for example, organosiloxanes having the general formula $\text{R}^4\text{O}(\text{SiR}^5_2\text{O})_t\text{H}$ wherein R^4 is a hydrogen or an alkyl or aryl group having up to 8 carbon atoms, each R^5 is the same or different and denotes a monovalent hydrocarbon group preferably having 1 to 18 carbon atoms or halogenated hydrocarbon group preferably having 1 to 18 carbon atoms and t is an integer of at least 2. Preferably R^5 denotes an alkyl group having from 1 to 6 carbon atoms and more preferably a methyl group. The value of t is preferably such that the average viscosity of the organopolysiloxanes does not exceed 200 mm²/s at 25°C.

[0026] Suitable organosiloxanes may have silicon-bonded hydroxyl groups or other silanol-forming hydrolysable groups which are in the polymer chain, but preferably these are present in end-groups. Organosiloxanes having terminal silicon-bonded hydroxyl groups are well known in the art and are commercially available. They can be made by techniques known in the art, for example, by hydrolysis of a chlorosilane, separation of the linear and cyclic material produced by the hydrolysis, and subsequently polymerising the linear material. Preferably suitable organosiloxanes have one silicon-bonded hydroxyl group in each terminal group and have at least 80% of the R^5 groups denote a methyl group. Suitable organosiloxanes for use as reagents in a polymerisation process in which the phosphazene base catalysts are used include organosiloxanes having terminal hydroxydiorganosiloxane units, e.g. hydroxydimethyl siloxane end-blocked polydimethylsiloxanes, hydroxydimethyl siloxane end-blocked polydimethyl poly-methylphenyl siloxane copolymers.

[0027] Starting materials for the ring-opening polymerisation reaction are cyclosiloxanes (also known as cyclic siloxanes). Cyclic siloxanes which are useful are well known and commercially available materials. They have the general formula $(\text{R}_2\text{SiO})_n$, wherein R denotes hydrogen or an optionally substituted alkyl, alkenyl, aryl, alkaryl or aralkyl group having up to 8 carbon atoms, n denotes an integer with a value of from 3 to 12. R can be substituted, e.g. by halogen such as fluorine or chlorine. The alkyl group can be, for example, methyl, ethyl, n-propyl, trifluoropropyl, n-butyl, sec-butyl, and tert-butyl. The alkenyl group can be, for example, vinyl, allyl, propenyl, and butenyl. The aryl and aralkyl groups can be, for example, phenyl, tolyl, and benzyl. The preferred groups are methyl, ethyl, phenyl, vinyl, and trifluoropropyl. Preferably at least 80% of all R groups are methyl or phenyl groups, most preferably methyl. It is most preferred that substantially all R groups are methyl groups. Preferably the value of n is from 3 to 6, most preferably 4 or 5. Examples of suitable cyclic siloxanes are octamethylcyclotetra-siloxane, decamethylcyclopentasiloxane, penta(methylvinyl)-cyclopentasiloxane, tetra(phenylmethyl)cyclotetrasiloxane and pentamethylhydrocyclopentasiloxane. One particularly suitable commercially available material is a mixture of octamethylcyclotetrasiloxane and decameth-

ylcyclopentasiloxane.

[0028] Where R is methyl, the compound is referred to as D_n; for example, where n = 4 the compound is called D₄.

[0029] We have found during preparation of the phosphazene base catalysts that air reacts very rapidly with the catalyst solutions giving a hazy material which eventually leads to an insoluble liquid phase. This is believed to be due to the reaction of the catalyst with water and/or CO₂ to form an insoluble hydroxide or carbonate salt. We have also found that this deactivation of the catalyst can be reversed e.g. by heating, purging with inert gas or subjecting the mixture to reduced pressure. This makes it possible to moderate or control the polymerisation reaction. This is particularly advantageous in view of the very rapid reaction which occurs when the reaction is not moderated. Because of the very low levels of catalyst employed in these reactions (which can be as low as 1 - 10ppm), the reaction with water and CO₂ needs to be taken into account to control the reaction and obtain reproducible results. By dissolving the phosphazene base in a large excess of water, in which it is very soluble and very stable, the catalyst activity becomes much more controllable and the polymers produced are of lower molecular weight. This is caused by the water acting as a catalyst inhibitor and also as an endblocker. The inhibiting effect of the water can be reduced by reducing the amount of water present e.g. by heating. At temperatures below 100°C the rate of polymerisation is relatively slow in the presence of water and/or CO₂, for example taking up to more than 24 hours to reach gum viscosity. At temperatures above 100°C (e.g. 100 - 150°C), polymerisation becomes much faster in the presence of water and/or CO₂, for example taking up to 5 - 60 minutes to reach gum viscosity. Such control of the reaction can also be achieved if the water is mixed with or replaced by alcohol (e.g. C₁-C₆ alcohols such as methanol or ethanol).

[0030] We have also found that polymerisation can be prevented by exposing a mixture of siloxane starting material and phosphazene base catalyst to air and/or CO₂. The polymerisation can then be initiated ("command polymerisation") simply by removing the air and/or CO₂ e.g. by heating the mixture (e.g. to 100°C - 140°C for a few minutes). A D₄ catalyst mixture (2 - 50ppm of catalyst) is stable in the presence of air and CO₂ at 20°C for extended periods (up to 7 days).

[0031] The reaction mixture is generally purged with inert gas, preferably nitrogen, prior to addition of the catalyst so as to remove any dissolved CO₂. Because of the extremely rapid reaction, the reaction mixture is vigorously mixed to ensure homogenous dispersion of the catalyst. Inadequate mixing can result in the catalyst being encapsulated in beads of gum as it is added to the reaction, and the catalyst then takes some time to diffuse out of the gum particles, giving a slower reaction.

[0032] The process according to the invention can be used to make gums of high molecular weight, for example from 1x10⁶ to 100x10⁶. The molecular weight of silicone polymers is limited by the concentration of end groups and in the absence of added endgroups is determined by the catalyst concentration. The catalyst used in the present invention has sufficient activity to afford polymers in a reasonable time at a low catalyst concentration even in the presence of fillers. Uses of these high molecular weight polymers with or without fillers include high consistency rubber, drag-reducing additives for oil pipelines, personal care products and sealants. We have found that phosphazene base catalysts when used at very low concentrations (2-500ppm) based on the weight of the siloxanes produce polymers with very high molecular weights (1,000,000-100,000,000) very quickly (10s-8h) at moderate to low temperatures (20-100°C). Molecular weight changes during polymerisation can be monitored by sampling the reaction during polymerisation, and analysing each sample by GPC (gel permeation chromatography) to determine the molecular weight. Polymers of very high molecular weights can be obtained almost immediately. The process can be used to produce ultra high molecular weight materials. This is by virtue of the very low catalyst concentrations needed for the polymerisation, with the result that the molecular weight of the polymer produced is dependent on the end group concentration which is equal to the catalyst concentration. However, we have found that at very low catalyst concentrations, such as 2ppm, the molecular weight obtained increases with reaction time. The process may be limited by diffusion of the catalyst, which is very slow in these high molecular weight polymers.

[0033] As an alternative to high molecular weight gums, the process according to the invention can also be used in equilibration reactions to produce silicone fluids, for example in the viscosity range at 25°C of from 1 to 150,000mm²/s. An endblocker is added in a proportion calculated to produce the desired molecular weight of polymer. Suitable endblockers are, for example, polysiloxanes in the molecular weight range from 160 upwards, in particular polydimethylsiloxanes of the general formula MD_xM where M is (CH₃)₃SiO_{1/2}, D is -Si(CH₃)₂O_{2/2}- and x has a value of from 0 to 20. The endblocker may have one or more functional groups such as hydroxy, vinyl or hydrogen. Water also acts as an endblocker, with the introduction of hydroxy functional groups.

[0034] In the process of the present invention, polymerisation may take place in the presence of a filler. The silicone polymer containing filler so produced is suitable for use as an electrical insulation grease, a sealant or as a reinforced polymer mixture useful in producing silicone elastomers.

[0035] Filler usable in the present invention, depending on the type, can act as a rheological control additive, reinforcer, extender or agent for imparting conductivity, etc. The filler may be a reinforcing filler such as fumed silica, precipitated silica, gel-formation silica, fumed titanium dioxide or carbon black; or an extending filler such as quartz powder, alumino silicate, aluminium oxide, zirconium silicate, magnesium oxide, zinc oxide, talc, diatomaceous earth,

iron oxide, calcium carbonate, clay, titanium dioxide, mica, glass powder or graphite.

[0036] Preferred fillers are finely divided reinforcing fillers for silicone elastomers. Examples of such fillers include carbon black; amorphous silica such as fumed silica, precipitated silica, gel-formation silica, diatomaceous earth, and fumed titanium dioxide. The reinforcing fillers have particle sizes in the colloidal range and specific surface areas greater than 50 m²/g, usually above 150m²/g. The most useful reinforcing filler is fumed silica with a specific surface area of at least 150m²/g. Silica fillers are preferably surface-treated by hydrophobising agents. Suitable hydrophobising agents include short polydimethyl siloxanes, hexamethyldisiloxane, silanes, silanol-endsblocked dimethyl siloxanes or fatty acids. Preferably hydrophobising agents are used which result in di- or triorgano silyl groups being present on the surface of the fillers.

[0037] The quantity of filler used depends on the type of filler and on the application of the silicone polymer. A strongly reinforcing filler such as fumed silica or precipitated silica will generally be employed at from 1 to 70 weight parts per 100 weight parts total siloxane. The highest reinforcing performance is obtained for this range of addition. Other fillers may be used at from 1 to 200 weight parts per 100 weight parts total siloxane, but the optimal quantity is appropriately determined by experiment. The filler may be a single filler or two or more fillers may be used simultaneously, whether they be all reinforcing, all extending or a mixture of both types of fillers.

[0038] The silicone polymers containing filler producable by the process of the present invention are useful in producing curable compositions which cure to silicone elastomers. They can be used in a manner similar to conventional mixtures of high viscosity polydiorganosiloxanes and fillers. A common method is the addition of an organic peroxide vulcanising agent to a filled polydiorganosiloxane mixture. The organic peroxide vulcanising agents suitable for use in silicone elastomers are well known. If the polydiorganosiloxane does not contain any vinyl radicals, it preferably is vulcanised with organic peroxides that are efficient in causing reactions in such polydiorganosiloxanes. Such organic peroxides are labelled "non-vinyl specific" and are represented by such organic peroxides as benzoylperoxide and 2,4-dichlorobenzoylperoxide. If the polydiorganosiloxane contains vinyl radicals, it can be vulcanised with either "non-vinyl specific" or "vinyl specific" organic peroxides. Representative of the vinyl specific organic peroxides are ditertiary-butyl peroxide and 2,5-bis-(tertbutylperoxy)-2, 5-dimethylhexane. The properties of the cured silicone elastomer can be altered by the type and amount of vulcanising agent used to cure the composition. Typical changes due to such choices are well recognised in the art. The organic peroxide vulcanising agent can be present in amounts from 0.1 to 5 parts by weight per 100 parts by weight of the filled polydiorganosiloxane, preferably from 0.5 to 2.0 parts by weight.

[0039] The embodiments of the process of this invention which afford a silicone polymer having hydroxyl endgroups can be further mixed with curing agents to yield curable compositions. A number of methods are known for combining hydroxyl-containing polydiorganosiloxane in an essentially anhydrous mixture with a curing agent to yield a one part curable composition. The compositions cure to silicone elastomers upon exposure to the atmosphere. Tri-functional and tetra-functional silanes are usable as crosslinking agents as well as short polymeric crosslinkers. Among the functional groups used are acetoxyl radicals, alkoxy radicals, amino radicals and amido radicals. Common catalysts for these systems include metal carboxylates, alkyl metal carboxylates, alkyl metal alkoxides and titanates. Preferred catalysts are stannous octoate, dibutyltindiacetate, dibutyltindilaurate, tetrabutyltitanate, dibutyltindimethoxide and tetraisopropyltitanate.

[0040] Silicone polymers containing two or more unsaturated monovalent aliphatic radicals per polymer molecule such as vinyl and allyl radicals can be combined with a curing agent comprising an organohydrogensiloxane having an average of more than two silicon-bonded hydrogen atoms per molecule, and a hydrosilylation catalyst, e.g. a platinum-containing catalyst in an amount sufficient to provide at least one part by weight platinum per million parts by weight polydiorganosiloxane. The organohydrogensiloxane is present in sufficient quantity to provide from at least one silicon-bonded hydrogen atom per unsaturated monovalent aliphatic radical in the polydiorganosiloxane. The polydiorganosiloxane in the mixture preferably contains from 0.01 to 2.0 mol percent unsaturated monovalent aliphatic radical.

[0041] The silicone polymers containing filler producable by the process of the present invention can also be combined with additives normally used with silicone polymer-filler mixtures such as thickeners, pigments, heat stability additives, oil resistance additives and flame retarding additives.

[0042] In step (ii) of the process of the present invention, the catalyst is neutralised to stabilise the product and prevent any further reaction. Suitable neutralising agents include acids such as acetic acid, silyl phosphate, polyacrylic acid chlorine substituted silanes, or silyl phosphonate. In theory, a 1:1 molar ratio of neutralising agent to catalyst will be sufficient to neutralise the catalyst; however, in practice a molar excess of neutralising agent is used, for example a molar ratio of neutralising agent to catalyst of 5:1 or above, depending on reaction conditions.

[0043] In step (iii) of the process of the present invention, the unstripped silicone polymer is stripped to remove volatile materials. Stripping may be effected under conditions used for stripping silicone polymers produced using conventional catalysts, for example at temperatures of from 120 to 200°C and under reduced pressure of 200 to 20000 Pa. However, silicone polymers produced by the process of the present invention can have lower volatile material content than silicone polymers produced using conventional catalysts by stripping the unstripped silicone polymer at temperatures at which unstripped silicone polymers produced using conventional catalysts will decompose. This is

possible due to the enhanced thermal stability of the unstripped silicone polymer produced during the present process, which is attributed to the very low levels of catalyst residue left remaining in the product after polymerisation. Thus, stripping can be effected at temperatures of 200°C and above, up to temperatures just below that at which the silicone polymer decomposes, for example at temperatures of up to 500°C depending on the particular silicone polymer to be stripped, for example up to 250, 300, 350, 400, 450 or 500°C. The higher the stripping temperature the more effective the removal of volatile materials. Stripping is also normally conducted under reduced pressure, for example from 200 to 20000 Pa. Stripping may be performed using conventional apparatus, for example using a rotating thin film evaporator or extruder.

[0044] The present invention will now be illustrated by way of example.

Example 1 - ring-opening polymerisation

[0045] Octamethyltetracyclosiloxane, 0.16% by weight (based on octamethyltetracyclosiloxane) of 4.5 mm²/s viscosity dimethylvinyl terminated polydimethylsiloxane, and 0.001% by weight (10ppm) of the phosphazene catalyst I above were reacted together in a twin screw extruder (diameter 24mm, length:diameter ratio 30:1) at a temperature of 160°C to afford a dimethylvinyl terminated polydimethylsiloxane having an average molecular weight of approximately 575,000.

Example 2 - neutralisation

[0046] The silicone polymer produced in Example 1 above was neutralised in the extruder by feeding silyl phosphonate into the extruder downstream from where the reaction of Example 1 took place in a molar ratio excess of 12.5.

Example 3 - stripping

[0047] A sample of the neutralised silicone polymer of Example 2 was stripped in a z-blade mixer at a temperature of 170°C and a pressure of 12150 Pa to remove volatile materials. The results are shown in Table 1 below.

Table 1

Initial weight (g)	Final weight (g)	Stripping time (hrs)	Weight loss (g)	% weight loss
12.795	12.755	2	0.04	0.40

Example 4 - thermogravimetric analysis

[0048] Samples of the neutralised silicone polymer of Example 2 (referred to as EX1) were tested by thermogravimetric analysis to determine their decomposition temperatures as follows. A sample of silicone polymer is placed on a load cell which records the mass of the sample. The temperature of the sample is gradually increased - as the decomposition temperature of the silicone polymer is reached depolymerisation starts to occur and silicone polymer converts back to cyclosiloxanes which are removed. The load cell records the weight of the sample throughout and hence the decomposition of the silicone polymer sample as a function of temperature. Thermogravimetric analysis was also performed on a dimethylvinyl terminated polydimethylsiloxane gum produced by ring-opening polymerisation of octamethyltetracyclosiloxane using a conventional potassium silanolate catalyst (referred to as COMP1). The results of the testing are shown in Table 2 below.

Table 2

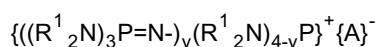
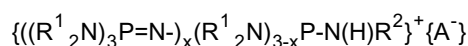
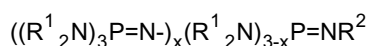
Sample	Decomposition temp. (°C)
EX1 sample 1	564
EX1 sample 2	567
COMP1 sample 1	381
COMP1 sample 2	376

Claims

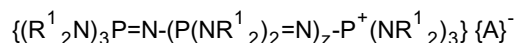
1. A process for producing a silicone polymer having a volatile material content of less than 1% by weight which

process comprises the sequential steps of (i) producing an unstripped silicone polymer by polymerisation of a linear silanol group containing siloxane by condensation polymerisation, or of a cyclosiloxane by ring-opening polymerisation, or of a mixture of said linear and cyclosiloxanes, with a phosphazene base in an amount of from 1 to 750ppm by weight based on weight of siloxane in the presence of at least 0.5mols of water per mol of phosphazene base and the presence or absence of a filler, (ii) neutralising the catalyst, and (iii) stripping the unstripped silicone polymer.

2. A process according to Claim 1 further **characterised in that** the silicone polymer has a volatile material content of 0.1% by weight or less.
3. A process according to Claim 1 or 2 further **characterised in that** the silicone polymer has a volatile material content of 0.01% by weight or less.
4. A process according to Claim 1, 2 or 3 further **characterised in that** the water is present in an amount of from 0.5 to 10 mols per mol of phosphazene base.
5. A process according to any preceding Claim further **characterised in that** the phosphazene base is present in an amount of from 2 to 200ppm by weight, based on the weight of siloxane, and the water is present in an amount of at least 1 mol per mol of phosphazene base.
6. A process according to any preceding Claim further **characterised in that** the phosphazene base is of one of the following general formulae:



or



in which R¹, which may be the same or different in each position, is hydrogen or an optionally substituted hydrocarbon group, or in which two R¹ groups bonded to the same N atom may be linked to complete a heterocyclic ring, R² is hydrogen or an optionally substituted hydrocarbon group, x is 1, 2 or 3, y is 1, 2, 3 or 4, z is an integer of from 1 to 10, and A is an anion.

7. A process according to any preceding Claim further **characterised in that** the cyclosiloxane is of the general formula (R₂SiO)_n, wherein R denotes hydrogen or an optionally substituted alkyl, alkenyl, aryl, alkaryl or aralkyl group having up to 8 carbon atoms, n denotes an integer with a value of from 3 to 12.
8. A process according to any preceding Claim further **characterised in that** the linear silanol group containing siloxane has the general formula R⁴O(SiR⁵₂O)_tH wherein R⁴ is a hydrogen or an alkyl or aryl group having up to 8 carbon atoms, each R⁵ is the same or different and denotes a monovalent hydrocarbon group preferably having 1 to 18 carbon atoms or halogenated hydrocarbon group and t is an integer of at least 2.
9. A process according to any preceding Claim further **characterised in that** an agent or conditions which inhibit catalyst activity is initially present, and polymerisation is then initiated by reducing the effect of the inhibiting agent or conditions.
10. A process according to Claim 9 further **characterised in that** the inhibiting agent is carbon dioxide and/or excess water, and **in that** the polymerisation reaction is initiated by heating.

11. A process according to any preceding Claim further **characterised in that** an endblocker is present in an amount calculated to result in a desired molecular weight range of polymer.

5 12. A process according to any preceding Claim further **characterised in that** polymerisation is terminated by adding a neutralising agent which prevents further catalyst activity.

10 13. A process according to any preceding Claim further **characterised in that** stripping is effected at a temperature of at least 200°C.

Patentansprüche

15 1. Verfahren zur Herstellung eines Siliconpolymers mit einem Gehalt an flüchtigem Material von weniger als 1 Gew.-%, wobei das Verfahren die aufeinander folgenden Schritte umfasst:

- 20 (i) Erzeugen eines nichtabgestrippten Siliconpolymers durch Polymerisation eines silanolgruppenhaltigen linearen Siloxans durch Kondensationspolymerisation oder eines Cyclosiloxans durch ringöffnende Polymerisation oder einer Mischung aus diesen linearen Siloxanen und Cyclosiloxanen mit einer Phosphazenenbase in einer Menge von 1 bis 750 Gew.ppm, bezogen auf das Gewicht von Siloxan, in Gegenwart von mindestens 0,5 mol Wasser pro mol Phosphazenenbase und in Anwesenheit oder Abwesenheit eines Füllstoffs,
- (ii) Neutralisieren des Katalysators und
- (iii) Abstreifen des nichtabgestrippten Siliconpolymers.

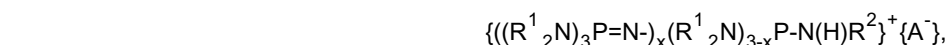
25 2. Verfahren nach Anspruch 1, ferner **dadurch gekennzeichnet, dass** das Siliconpolymer einen Gehalt an flüchtigem Material von 0,1 Gew.-% oder weniger aufweist.

30 3. Verfahren nach Anspruch 1 oder 2, ferner **dadurch gekennzeichnet, dass** das Siliconpolymer einen Gehalt an flüchtigem Material von 0,01 Gew.-% oder weniger aufweist.

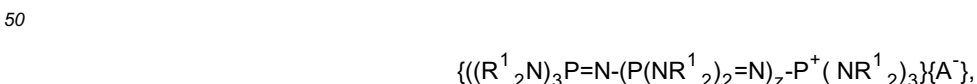
35 4. Verfahren nach Anspruch 1, 2 oder 3, ferner **dadurch gekennzeichnet, dass** das Wasser in einer Menge von 0,5 bis 10 mol pro mol Phosphazenenbase vorhanden ist.

5. Verfahren nach einem der vorstehenden Ansprüche, ferner **dadurch gekennzeichnet, dass** die Phosphazenenbase in einer Menge von 2 bis 200 Gew.-ppm, bezogen auf das Gewicht von Siloxan, vorhanden ist und das Wasser in einer Menge von mindestens 1 mol pro mol Phosphazenenbase vorhanden ist.

6. Verfahren nach einem der vorstehenden Ansprüche, ferner **dadurch gekennzeichnet, dass** die Phosphazenenbase eine der folgenden allgemeinen Formeln ist:



oder

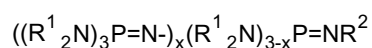


55 in welchen R¹, das in jeder Stellung gleich oder unterschiedlich sein kann, Wasserstoff oder eine optional substituierte Kohlenwasserstoffgruppe ist oder in welchen zwei R¹-Gruppen, die an dasselbe N-Atom gebunden sind, miteinander verknüpft sein können, um einen heterocyclischen Ring zu vervollständigen, R² gleich Wasserstoff oder eine optional substituierte Kohlenwasserstoffgruppe ist, x gleich 1, 2 oder 3 ist, y gleich 1, 2, 3 oder 4 ist, z eine ganze Zahl von 1 bis 10 ist und A ein Anion ist.

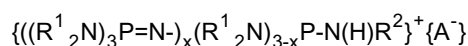
7. Verfahren nach einem der vorstehenden Ansprüche, ferner **dadurch gekennzeichnet, dass** das Cyclosiloxan der allgemeinen Formel $(R_2SiO)_n$ entspricht, worin R Wasserstoff oder eine optional substituierte Alkyl-, Alkenyl-, Aryl-, Alkaryl- oder Aralkylgruppe mit bis zu 8 Kohlenstoffatomen bedeutet, n eine ganze Zahl mit einem Wert von 3 bis 12 bedeutet.
8. Verfahren nach einem der vorstehenden Ansprüche, ferner **dadurch gekennzeichnet, dass** das lineare silanolgruppenhaltige Siloxan der allgemeinen Formel $R^4O(SiR^5_2O)_tH$ entspricht, worin R^4 ein Wasserstoff oder eine Alkyl- oder Arylgruppe mit bis zu 8 Kohlenstoffatomen ist, jedes R^5 gleich oder unterschiedlich ist und eine monovalente Kohlenwasserstoffgruppe, die vorzugsweise 1 bis 18 Kohlenstoffatome aufweist, oder eine halogenierte Kohlenwasserstoffgruppe bedeutet und t eine ganze Zahl von mindestens 2 ist.
9. Verfahren nach einem der vorstehenden Ansprüche, ferner **dadurch gekennzeichnet, dass** ein Mittel oder Bedingungen, die katalytische Aktivität hemmen, zu Beginn vorhanden sind und Polymerisation dann durch Herabsetzen der Wirkung des inhibierenden Mittels oder der inhibierenden Bedingungen initiiert wird.
10. Verfahren nach Anspruch 9, ferner **dadurch gekennzeichnet, dass** das inhibierende Mittel Kohlendioxid und/oder überschüssiges Wasser ist und dadurch, dass die Polymerisationsreaktion durch Erwärmen initiiert wird.
11. Verfahren nach einem der vorstehenden Ansprüche, ferner **dadurch gekennzeichnet, dass** ein Endblockierungsmittel in einer Menge vorhanden ist, die berechnet wird, um in einem Polymer mit einem gewünschten Molekulargewichtsbereich zu resultieren.
12. Verfahren nach einem der vorstehenden Ansprüche, ferner **dadurch gekennzeichnet, dass** die Polymerisation durch Hinzufügen eines Neutralisationsmittels beendet wird, das weitere katalytische Aktivität verhindert.
13. Verfahren nach einem der vorstehenden Ansprüche, ferner **dadurch gekennzeichnet, dass** das Abstreifen bei einer Temperatur von mindestens 200°C bewirkt wird.

Revendications

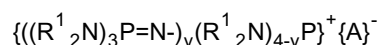
1. Procédé pour la production d'un polymère de silicone ayant une teneur en matière volatile inférieure à 1 % en poids, lequel procédé comprend les étapes successives de (i) production d'un polymère de silicone non épuré par polymérisation d'un siloxane linéaire contenant un groupe silanol par polymérisation par condensation, ou d'un cyclosiloxane par polymérisation par ouverture de cycle, ou d'un mélange desdits linéaire et cyclosiloxane, avec une base de phosphazène dans une quantité de 1 à 750 ppm en poids rapportée au poids de siloxane en présence d'au moins 0,5 mol d'eau par mole de base de phosphazène et en présence ou en l'absence d'une charge, (ii) neutralisation du catalyseur, et (iii) épuration du polymère de silicone non épuré.
2. Procédé selon la revendication 1, **caractérisé en outre en ce que** le polymère de silicone présente une teneur en matière volatile de 0,1 % en poids ou inférieure.
3. Procédé selon la revendication 1 ou 2, **caractérisé en outre en ce que** le polymère de silicone présente une teneur en matière volatile de 0,01 % en poids ou inférieure.
4. Procédé selon la revendication 1, 2 ou 3 **caractérisé en outre en ce que** l'eau est présente en une quantité de 0,5 à 10 mol par mole de base de phosphazène.
5. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en outre en ce que** la base de phosphazène est présente dans une quantité de 2 à 200 ppm en poids, rapportée au poids du siloxane, et l'eau est présente dans une quantité d'au moins 1 mol par mole de base de phosphazène.
6. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en outre en ce que** la base de phosphazène est une base des formules générales suivantes :



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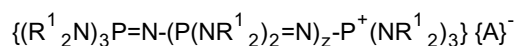


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ou

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dans lesquelles R¹, qui peuvent être identiques ou différents dans chaque position, est un atome d'hydrogène ou un groupe hydrocarboné facultativement substitué, ou dans lesquelles deux groupes R¹ liés au même atome N peuvent être liés pour compléter un cycle hétérocyclique, R² est un atome d'hydrogène ou un groupe hydrocarboné facultativement substitué, x est égal à 1, 2 ou 3, y est égal à 1, 2, 3 ou 4, z est un nombre entier de 1 à 10 et A est un anion.

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7. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en outre en ce que** le cyclosiloxane est de la formule générale (R₂SiO)_n, où R indique un atome d'hydrogène ou un groupe alkyle, alcényle, aryle, alkaryle ou aralkyle facultativement substitué ayant jusqu'à 8 atomes de carbone, n indique un nombre entier avec une valeur de 3 à 12.

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8. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en outre en ce que** le siloxane linéaire contenant un groupe silanol présente la formule générale R⁴O(SiR⁵₂O)_tH, dans laquelle R⁴ est un atome d'hydrogène ou un groupe alkyle ou aryle ayant jusqu'à huit atomes de carbone, chaque R⁵ est identique ou différent et indique un groupe hydrocarboné monovalent ayant de 1 à 18 atomes de carbone ou un groupe hydrocarboné halogéné et t est un nombre entier d'au moins 2.

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9. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en outre en ce qu'un** agent ou des conditions qui inhibent l'activité du catalyseur est initialement présent, et la polymérisation est ensuite initiée en réduisant l'effet de l'agent ou des conditions d'inhibition.

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10. Procédé selon la revendication 9, **caractérisé en outre en ce que** l'agent d'inhibition est du dioxyde de carbone et/ou de l'eau en excès, et **en ce que** la réaction de polymérisation est initiée par chauffage.

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11. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en outre en ce qu'un** agent bloquant terminal est présent dans une quantité calculée pour résulter en un intervalle souhaité du poids moléculaire du polymère.

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12. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en outre en ce que** la polymérisation est achevée en ajoutant un agent de neutralisation qui empêche en outre l'activité du catalyseur.

13. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en outre en ce que** l'épuration est réalisée à une température d'au moins 200°C.

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